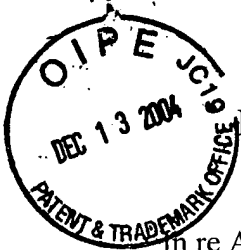




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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Applicant:

Franklin E. Parks

Filed: August 13, 2001

Serial No.: 09/928,764

For: Polyurethane Films and Dispersions
For the Preparation Thereof

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Group Art Unit: 1711

Examiner: Rabon A. Sergent

Attorney Docket No.: 019131-02700
(44446 US)

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APPEAL BRIEF

Board of Patent Appeals and Interferences
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Appellant hereby submits this Appeal Brief, in triplicate, with the requisite fee as set forth in 37 C.F.R. § 1.17(c). A Notice of Appeal was timely filed on September 8, 2004. This Appeal Brief is accordingly timely filed. The requisite fee set forth in 37 C.F.R. § 1.17(c) may be debited from the Deposit Account 12-1322 (019131-02700).

I. REAL PARTY IN INTEREST

The real party in interest in this appeal is Dow Global Technologies, Inc., a corporation formed under the laws of the United States, located at 2030 Dow Center, Midland, Michigan, 48642, to whom this application has been assigned.

II. RELATED APPEALS AND INTERFERENCES

No related appeals or interferences exist.

III. STATUS OF CLAIMS

As originally filed, this application contained Claims 1-16. During prosecution of the application, Claims 17-41 were added to the application. Claims 1, 5, 7-9, 11-12, 24 and 27-41 are now pending in this application. These claims have been rejected by the Examiner, on grounds discussed herein.

Accordingly, the claims on appeal are Claims 1, 5, 7-9, 11-12, 24 and 27-41. A copy of the claims on appeal is set forth in the *Appendix*. Each of these claims stands finally rejected for which Appellant brings the present appeal to the Board.

IV. STATUS OF AMENDMENTS

Claim 36 was amended subsequent to the final rejection to correct a grammatical error. No other amendments were made prior to the final rejection. The Examiner declined to enter the amendment to Claim 36.

V. SUMMARY OF CLAIMED SUBJECT MATTER

Claim 1 is a product-by-process claim directed to a polyurethane film prepared from a polyurethane dispersion. The dispersion is formed in at least two steps. In the first step, a non-ionic polyurethane prepolymer is formed (P. 3, L. 28; P. 4, L. 30) from a MDI diisocyanate, having a P,P'-isomer content from 99 to 90 percent (P. 5, LL. 4-10) and an active hydrogen containing material (P. 5, LL. 26-29). In the second step, an aqueous dispersion of the prepolymer is formed (P.3, ll. 28-29).

The claimed film exhibits markedly higher tensile strength. In each of Claims 1, 5, 7-12, 24-25 and 30-38, the MDI diisocyanate is recited as having a content of P,P'-isomer from 99 to 90 percent. In Claims 27, 29, 39 and 41, the content of P,P'-isomer is recited as being 98 percent. In Claims 28 and 40, the content of P,P'-isomer is recited as being 94 percent. Appellant has demonstrated that films prepared from dispersions employing the claimed percentage of P,P'-isomer exhibit markedly higher tensile strength. Note the reported tensile strength of the films reported in Table I [Examples 1, 2 and 4 (wherein the 4,4' isomer content of the MDI diisocyanate is 98 percent) in contrast to Example 3 the 4,4' isomer content of the MDI diisocyanate is about 75 percent.] (The MDI of Example 3 is an approximate 50:50 weight ratio of MDI having a 4,4' isomer content of 98 percent and a MDI having a 4,4' isomer content of 50 percent). The tensile strength of the resulting polyurethane is dramatic. Compare 2604 psi of Example 3 with 5830, 4342 and 4976 psi of Examples 1, 2 and 4, respectively. (PP. 11-13.)

Independent Claim 9 is directed to a method for preparing a polyurethane film in three steps. In the first step, the non-ionic polyurethane prepolymer is prepared (P. 3, L. 28; P. 4, L. 30) from a MDI diisocyanate, having a P,P'-isomer content from 99 to 90 percent (P. 5, LL. 4-10), and an active hydrogen containing material. In the second step, the prepolymer is dispersed in water. (P. 3, LL. 26-29.) In the third step, the dispersion is applied to a substrate.

Independent Claim 24 is a product-by-product claim directed to an aqueous polyurethane dispersion formed in at least two steps. In the first step, a nonionic polyurethane prepolymer is formed from a MDI diisocyanate, having a P,P'-isomer content from 99 to 90 percent, and an active hydrogen containing material. In the second step, an aqueous dispersion of the prepolymer is formed.

VI. GROUND OF REJECTION TO BE REVIEWED ON APPEAL

The issues on appeal are premised on the grounds of rejection set forth in the Final Office Action dated March 8, 2004. The issues are as follows:

- A. Whether Claims 1, 5, 7, 9, 24, 25, and 27-41 are anticipated under 35 U.S.C. § 102 (e) by U.S. Patent No. 5,959,027 (“*Jakubowski*”);
- B. Whether Claims 1, 5, 7, 9, 24, 25 and 27-41 are anticipated under 35 U.S.C. § 102(a) by *WO 98/41552*;
- C. Whether Claims 1, 5, 7, 9, 11, 24, 25 and 27-41 are anticipated under 35 U.S.C. § 102(a) by *WO 98/41554*; and
- D. Whether Claims 8, 11 and 12 are unpatentable under 35 U.S.C. § 103(a) over *WO 98/41552* or *WO 98/41554*, each in view of U.S. Patent No. 6,389,602 (“*Alsaffar*”).

VII. ARGUMENT

A. Rejection of Claims 1, 5, 7, 9, 24, 25, and 27-41 Over *Jakubowski*.

Jakubowski discloses a polyurethane/urea/thiourea latex prepared from an emulsion. *Jakubowski* does not disclose use of a MDI wherein the P,P'-isomer content of the MDI is between 90 to 99 percent. The Examiner's rejection is premised on the recitation in *Jakubowski* that a suitable diisocyanate is 4,4'-diphenylmethane diisocyanate (col. 3, ll. 7-8). The Examiner contends that “applicants’ claimed P,P'-isomer content is met by *Jakubowski* because the processing of 4,4'-MDI inherently yields an insignificant quantity of other isomers; as a result it is reasonable to conclude that the P,P'-isomer content is slightly below 100 percent and meets the applicants’ claimed percent values.” (Paragraph 4 of Final Office Action.) The Examiner has provided no basis upon which to conclude that 4,4'-MDI contains such “insignificant” amounts of impurities to render a P,P'-isomer content of 99 percent, much less 98 (Claim 29) or 94 (Claim 40) percent. Even if such “insignificant” quantities were disclosed, an “insignificant”

quantity would imply trace amounts of impurities at ppm levels. 1% is equal to 10,000 ppm and 10,000 ppm is not considered an “insignificant” quantity.

In any event, *Jakubowski* only discloses the P,P'-isomer which the Examiner concedes is the high purity isomer. A high purity isomer would have a P,P'-isomer content in excess of 99 percent. Methods of making high purity P,P'-isomer polyisocyanates are well documented in the prior art. Note, for instance, U.S. Patent No. 4,118,410, copy attached as *Exhibit A*, wherein it is reported that the 4,4'-isomer which is “considerably higher than 99%” is obtained by crystallization, distillation and displacement washing. *Witness*, for instance, the bridging paragraph of columns 1 and 2 and col. 4, ll. 11-33. *See further* Great Britain No. 1,263,439, copy attached as *Exhibit B*, and in particular p. 3, ll. 72-83. There is no reason to conclude that the 4,4'-isomer of *Jakubowski* would have a 4,4'-isomer content less than 99% and the prior art clearly refutes the Examiner's contention that highly pure P,P'-isomers would have “trace amounts” of impurities of 1% or more.

Jakubowski therefore does not anticipate Claims 1, 5, 7, 9, 24, 25 nor 27-41. Anticipation is established only if all the elements of an invention, as stated in a patent claim are identically set forth in a single prior art reference. *Mehl/Biophile International Corp. v. Milgraum*, 192 F.3d 1362, 1365, 52 USPQ2d 1303, 1306 (Fed. Cir. 1999) (“To anticipate, a single reference must teach every limitation of the claimed invention.”); *In re Donohue*, 766 F.2d 531, 534, 226 USPQ 619, 621 (Fed. Cir. 1985) (“an anticipation rejection requires a showing that each limitation of a claim must be found in a single reference, practice, or device”).

Further, *Jakubowski* does not appreciate the improvement in tensile strength, as illustrated in the Table on page 13 of Appellant's specification. In the Examples of *Jakubowski*, the P,P' isomer content of the MDI component is at best no greater than 76 percent, i.e., the same

system set forth in Example 3 on page 13 of Appellant's specification. (Note that the isocyanate of *Jakubowski* is derived from a 50:50 mixture of 4, 4'-diisocyanatodiphenylmethane and 2, 4'-diisocyanatodiphenylmethane, col. 5, ll. 20-25 as well as col. 7, ll. 27-30. *See*, for instance, lines 19-29 of column 5 wherein a 50:50 mixture of 4,4' and 2,4' isomers is disclosed.)

1. Claims 27-29 and 39-41 Should Not Be Grouped with the Other Claims.

The Examiner's rejection of Claims 27, 29, 39 and 41 (reciting a P,P'-isomer content of 98 percent) and Claims 28 and 40 (reciting a maximum P,P'-isomer content of 94 percent) is even more tenuous since the prior art clearly refutes the Examiner's contention that highly pure P,P'-isomers would have "trace amounts" of impurities within the claimed limitations. The upper limitation of 98 percent, much less 94 percent, set forth in these dependent claims is outside of the teachings of *Jakubowski*.

Claims 1, 5, 7, 9, 24, 25 and 27-41 are therefore not anticipated by *Jakubowski*. The rejection of Claims 1, 5, 7, 9, 24, 25 and 27-41 over *Jakubowski* should therefore be *reversed*.

B. Rejection of Claims 1, 5, 7, 9, 24, 25, and 27-41 Over WO 98/41552.

WO 98/41552 suffers from the same deficiencies as *Jakubowski*, discussed *supra*. In fact, *WO 98/41552* is merely a published PCT equivalent of *Jakubowski*. Note the international filing date of *WO 98/41552* is equivalent to the U.S. filing date of *Jakubowski* and both *WO 98/41552* and *Jakubowski* both claim priority to provisional application serial no. 60/039,194, filed March 17, 1997.

1. Claims 27-29 and 39-41 Should Not Be Grouped with the Other Claims.

The Board should separately consider the impropriety of the rejection of Claims 27-29 and 39-41 over *WO 98/41552* from the remaining claims. The rationale discussed above under Section VII 1 (i.) applies equally here to the rejection of the dependent claims over *WO 98/41552*.

C. Rejection of Claims 1, 5, 7, 9, 11, 24, 25, and 27-41 Over *WO 98/41554*.

WO 98/41554 discloses polyurethane latexes derived from a polyisocyanate and polyol. *WO 98/41554* suffers from the same deficiencies as *WO 98/41552* and *Jakubowski*, discussed *supra*. In particular, *WO 98/41554* does not disclose use of a MDI wherein the P,P'-isomer content of the MDI is between 90 to 99 percent. The Examiner's rejection is premised on the recitation in *WO 98/41554* that a suitable diisocyanate is 4,4'-diphenylmethane diisocyanate (p. 10, ll. 4-5 and 10.). The Examiner's contention that 4,4'-MDI inherently yields an "insignificant quantity of other isomers" (paragraph 8 of Office Action of March 8, 2004) is not supported. In fact, the prior art discussed *supra* clearly shows that high purity 4,4'-MDI contains much greater than 99 percent of P,P'-isomer content.

1. Claims 27-29 and 39-41 Should Not Be Grouped with the Other Claims.

The Board should separately consider the impropriety of the rejection of Claims 27-29 and 39-41 over *WO 98/41554* from the remaining claims. The rationale discussed above under Section VII 1 (i.) and Section VII 2 (i.) applies equally here to the rejection of the dependent claims over *WO 98/41554*.

D. Rejection of Claims 8 and 11-12 Over *WO 98/41552* or *98/41554* In View of *Alsaffar*.

The deficiencies of both *WO 98/41552* and *WO 98/41554* are discussed *supra*. *Alsaffar* is directed to condoms and gloves made of films of polyurethanes. The MDI polyisocyanates claimed by Appellant are not disclosed in *Alsaffar*. Since neither *WO 98/41552*, *WO 98/41554* and *Alsaffar* fail to disclose use of a MDI wherein the P,P'-isomer content of the MDI is between 90 to 99 percent, the rejection should be *reversed*.

VIII. CONCLUSION

The rejections of:

Claims 1, 5, 7, 9, 24, 25, and 27-41 as anticipated under 35 U.S.C. § 102 (e) by *Jakubowski*;

Claims 1, 5, 7, 9, 24, 25 and 27-41 as anticipated under 35 U.S.C. § 102(a) by *WO 98/41552*;

Claims 1, 5, 7, 9, 11, 24, 25 and 27-41 as anticipated under 35 U.S.C. § 102(a) by *WO 98/41554*; and

Claims 8, 11 and 12 as unpatentable under 35 U.S.C. § 103(a) over *WO 98/41552* or *WO 98/41554*, each in view of *Alsaffar*

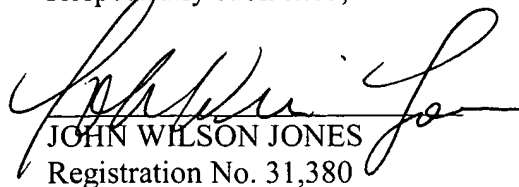
are improper for the reasons discussed herein. Accordingly, Claims 1, 5, 7-9, 11-12, 24-25 and 27-41 are in condition for allowance.

A decision of the Board consistent with this showing is earnestly requested.

Respectfully submitted,

Date:

12/08/2004

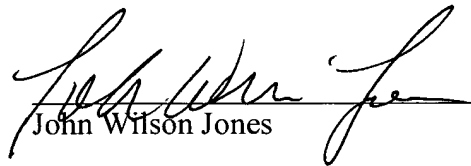

JOHN WILSON JONES
Registration No. 31,380



LOCKE LIDDELL & SAPP LLP
3400 JP Morgan Chase Tower
600 Travis Street
Houston, Texas 77002-3095
Telephone: (713) 226-1142
Facsimile: (713) 229-2570

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Board of Patent Appeals and Interferences, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450 on December 8, 2004.


John Wilson Jones



CLAIMS APPENDIX

CLAIMS ON APPEAL

1. A polyurethane film comprising a film prepared from a polyurethane dispersion, the dispersion being prepared from a non-ionic polyurethane prepolymer, and the prepolymer being prepared from a polyurethane prepolymer formulation including a MDI diisocyanate, the MDI having a P,P'-isomer content from 99 to 90 percent and an active hydrogen containing material wherein:

the dispersion is formed in a two or more step process wherein,

- (1) in a first step the prepolymer is formed and, in a subsequent step,
- (2) an aqueous dispersion of the prepolymer is formed.

5. The polyurethane film according to Claim 29 wherein the anionic surfactant is sodium dodecyl benzene sulfonate.

7. The polyurethane film according to Claim 1 wherein the dispersion has a solids content of from 5 to 60 weight percent.

8. The film of Claim 1, wherein the film has a shape of a glove, a condom, an angioplasty balloon, a medical bag or a catheter.

9. A process for preparing a polyurethane film comprising the steps of:

- (a) preparing a non-ionic polyurethane prepolymer;
- (b) dispersing the prepolymer in water; and then
- (c) applying the dispersion to a substrate as a film;

wherein the prepolymer is prepared from a polyurethane prepolymer formulation including a MDI diisocyanate, the MDI having a P,P'-isomer content from 99 to 90 percent and an active hydrogen containing material.

11. The process according to Claim 9 wherein step (c) comprises dipping, thermal coagulation, casting, electrodeposition, or a combination thereof.

12. The process of Claim 9 wherein the shape of the substrate is such that the resulting film is in the shape of a glove, condom, angioplasty balloon, medical bag, medical tubing, or catheter.

24. An aqueous polyurethane dispersion, comprising the product of dispersing in water a nonionic polyurethane prepolymer prepared from a prepolymer formulation including an MDI diisocyanate, the MDI having a P,P'-isomer content from 99 to 90 percent wherein the dispersion is formed in a two or more step process wherein:

- (1) in a first step the prepolymer is formed and, in a subsequent step,
- (2) an aqueous dispersion of the prepolymer is formed.

25. The dispersion of Claim 24, wherein the dispersion has a solids content of from about 5 to about 60 weight percent.

27. The polyurethane film of Claim 1, wherein the P,P'-isomer content of the MDI diisocyanate is from about 98 to about 92 percent.

28. The polyurethane film of Claim 27, wherein the P,P-isomer content of the MDI diisocyanate is about 94 percent.

29. The polyurethane film of Claim 27, wherein the P,P-isomer content of the MDI diisocyanate is about 98 percent.

30. The polyurethane film of Claim 1, wherein the aqueous dispersion of the prepolymer is formed in the presence of an anionic surfactant.

31. The polyurethane film of Claim 1, wherein the two or more step process for forming the dispersion occurs in the substantial absence of an organic solvent.

32. The polyurethane film of Claim 1, wherein the particle size of the particulates in the dispersion is from 0.9 microns to about 0.05 microns.

33. The process of Claim 9, wherein the prepolymer is dispersed in water in the presence of an anionic surfactant.
34. The process of Claim 9, wherein the particle size of the particulates in the dispersion being from 0.9 microns to about 0.05 microns.
35. The process of Claim 9, wherein both steps (a) and (b) occur in the substantial absence of an organic solvent.
36. The aqueous polyurethane dispersion of Claim 24, wherein the prepolymer formulation further comprising a mixture of diols.
37. The aqueous polyurethane dispersion of Claim 24, wherein the aqueous dispersion of the prepolymer is formed in the presence of an anionic surfactant.
38. The aqueous polyurethane dispersion of Claim 24, wherein both steps (1) and (2) occur in the substantial absence of an organic solvent.
39. The aqueous polyurethane dispersion of Claim 24, wherein the P,P'-isomer content of the MDI diisocyanate is between about 98 to about 92 percent.
40. The aqueous polyurethane dispersion of Claim 38, wherein the P,P'-isomer content of the MDI diisocyanate is about 94 percent.
41. The aqueous polyurethane dispersion of Claim 38, wherein the P,P'-isomer content of the MDI diisocyanate is about 98 percent.

EVIDENCE APPENDIX

Exhibit A. U.S. Patent No. 4,118,410.

Exhibit B. Great Britain no. 1,263,439.

The following is an explanation for the submission of *Exhibit A* and *Exhibit B*, pursuant to 37 CFR 41.33(d)(1):

The Examiner did not articulate his rationale for concluding that the 4,4'-MDI of the cited references inherently yielded an insignificant quantity of other isomers until the Final Rejection of 8 March 2004. Compare paragraph 4 of Final Rejection with paragraphs 5-7 of Office Action of 17 September 2003. Submission of *Exhibit A* and *Exhibit B* is desired to refute the Examiner's contentions raised in paragraph 4 of the Final Rejection.

RELATED PROCEEDINGS APPENDIX

None.

AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Superintending Examiner acting for the Comptroller General dated the third day of October 1974, under Section 14, of the Patents Act, 1949.

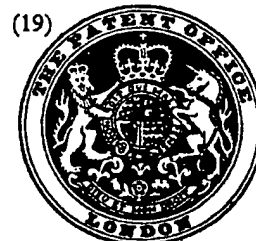
PATENT SPECIFICATION

(11) 1 263 439

1 263 439

NO DRAWINGS

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(32) Filed 7 May 1969 in
(33) Germany (DT)
(45) Complete Specification published 9 Feb. 1972
(51) International Classification C07c 119/04
(52) Index at acceptance
C2C 220 227 22Y 30Y 349 622 632 707 714 MH
(72) Inventor PETER FISCHER



(54) A PROCESS FOR THE PRODUCTION OF ISOCYANATES

- (71) We, **FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT**, of 509, Leverkusen, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to a process for the production of isocyanates.
- 15 4,4'-Diisocyanato diphenylmethane, a starting material for the production of polyurethane elastomers and coatings, is commercially produced from 4,4'-diamino diphenylmethane by reaction with phosgene in inert solvents, usually in chlorobenzene. The diamine is obtained by condensation in aqueous hydrochloric acid solution of aniline and formaldehyde from which a polyamine mixture containing the diamine as the main constituent is formed. The compounds with more than two nuclei can be separated off at the amine stage. Unfortunately, distillation of the polyamine mixture is complicated by the high boiling point and the solidification point of 4,4'-diamino diphenylmethane (92° C). Thus, polyamines left in the residue are solid at room temperature and are difficult to handle or the distillation involves considerable losses if diamines are left in the amine residue in order to improve the flow properties.
- 30 It is much simpler to react the polyamine mixture prepared from aniline and formaldehyde as a whole with phosgene to form a polyisocyanate mixture and then to distil off 4,4'-diisocyanato diphenylmethane from this polyisocyanate mixture. The disadvantage of this process is that the unwanted higher-
- functional polyamines are also reacted with phosgene and are lost either as isocyanates or as by-products which are derived from the isocyanates, for example as carbodiimides and carbodiimide-isocyanate adducts. A 4,4'-diisocyanato diphenylmethane which is at least 98% pure can not be obtained in this way because diamines with an NH₂ in the ortho-position, based on the methylene group in the diphenylmethane structure, are also formed during the aniline-formaldehyde condensation, and because the 2,2'- and 2,4'-diisocyanato diphenylmethane distil over together with the 4,4'-isomer during the distillation of a mixture.
- 55 It is an object of the present invention to provide a method of obtaining at least 98% by weight pure 4,4'-diisocyanato diphenylmethane from the phosgenation product of a polyamine mixture of this kind which has been obtained by condensing aniline and formaldehyde and also provides valuable starting materials for the production of polyurethanes which are also simultaneously obtained from the phosgenation products of the higher-functional polyamines.
- 65 The invention provides a process for the production both of (II) at least 98% by weight pure 4,4'-diphenylmethane diisocyanate and a polyphenylpolymethylene - polyisocyanate mixture (III) from a polyisocyanate mixture (I) which has been obtained by condensation of aniline and formaldehyde, followed by phosgenation of the condensation product, wherein the polyisocyanate mixture (I) is separated by fractional distillation into a fraction A which consists mainly of isomeric diphenylmethane diisocyanates, and a fraction B which, in addition to isomeric diphenyl

methane diisocyanates, consists of polyisocyanates containing more than two aromatic nuclei, and in which fraction A is then separated by fractional distillation into a fraction C consisting of 2,2', 2,4'- and 4,4'-diphenylmethane diisocyanates, and a fraction D at least 98% by weight of which consists of 4,4'-diphenylmethane diisocyanate and into a residue E comprising material formed as a result of high temperature polymerisation and in which fraction C is mixed with at least part of fraction B to produce a mixture having a K-value (as herein defined) of greater than 1.3 which mixture is product (III); the product (II) being fraction D.

If desired fraction C may be mixed not only with at least part of fraction B but also with residue E to give product (III).

Various components in the polyisocyanate mixture (I) used as starting material in the process according to the invention can be quantitatively detected by gas chromatography. These components include *inter alia* the dinuclear isomers 2,4'-diphenylmethane diisocyanate and 4,4'-diphenylmethane diisocyanate and the trinuclear isomers 1 - (4-isocyanato phenylmethyl) - 3 - (2 - isocyanato phenylmethyl) - 4 - isocyanato benzene (3 K I) and 1,3 - di - (4 - isocyanato phenylmethyl) - 4 - isocyanato benzene (3 K II). In order to clarify the description, the ratio between the gas-chromatographically determined concentrations of the dinuclear 2,4'- and 4,4'-isomers will be referred to simply as *a*, and the ratio between the concentrations of the trivalent isomers 3 K I:3 K II referred to simply as *b*.

In a polyisocyanate mixture of the kind which is obtained by the condensation of aniline and formaldehyde, followed by phosgenation of the condensation product, the ratio of ortho- and para-compounds and the ratio of dinuclear to higher-nuclear compounds vary within wide limits depending upon the concentration of the starting materials, aniline, formaldehyde and acid catalyst, upon the temperature and upon the pH value at which condensation is carried out. However, the ratio between the ratios *a* and *b* defined above remains equal to a factor K, largely independent of the above reaction conditions. The value for K is between 0.4 and 1.2. In contrast, the ratio is greater by at least 0.1 in the polyisocyanate mixtures (III) prepared by the process according to the invention which have a higher concentration of 2,4'-isomers than the undistilled starting material. The result of this is that, in the polyisocyanate mixtures (III) prepared by the process according to the invention, the factor K is always greater than 1.3 and usually lies between 1.4 and 100.

Apart from the polyisocyanate mixture thus defined, it is also possible by the process according to the invention to produce at least

98% by weight pure 4,4'-diphenylmethane diisocyanate (II).

The starting material is a polyamine mixture which is prepared from aniline and formaldehyde which is then reacted with phosgene in an inert solvent, for example in chlorobenzene, to give the polyisocyanate mixture (I). Accordingly, there is no need to prepare two different condensation products from aniline and formaldehyde, one for the production of 4,4'-diisocyanato diphenylmethane and the other for the production of polyisocyanate mixtures which are liquid at room temperature and have diphenylmethane structures.

The composition of the starting material, a mixture of polyisocyanates of the diphenylmethane series, is not critical for the practical application of the process. Polyisocyanate mixtures with a diisocyanate content of from 40 to 80% by weight and a 2,4'-isomer content in the diisocyanate component of from 1 to 40% by weight, are readily obtained on a large scale, although it is preferred to use polyisocyanate mixtures containing from 50 to 70% by weight diisocyanate and with from 4 to 8% by weight of 2,4'-isomers in the diisocyanate component. The preparation of polyamine mixtures which with phosgene yield polyisocyanate mixtures such as these is advantageous in regard to volume-time yield, acid, alkali and energy consumption.

As in the subsequent distillations, the first stage of the process in which a fraction A, namely a mixture of 2,2', 2,4'- and 4,4'-diisocyanate diphenylmethane, is separated from the starting material by distillation, has to be carried out in a manner which prevents the isocyanate groups from being degraded by heat. Apparatus which is suitable for this purpose includes falling-film evaporators operated continuously under a vacuum below 15 Torr, through which some of the material to be evaporated is repeatedly circulated by means of rotary pumps. Up to 70% by weight of diisocyanate can be distilled off, depending upon the diisocyanate content of the starting material. The operation can be controlled by monitoring the viscosity of the concentrate from which diisocyanate has been removed, namely the fraction B. The viscosity of the concentrate is between 200 and 10,000 cP/25° C, depending upon the quantity of diisocyanate mixture distilled off. The concentrate B from which diisocyanate has been removed does not show such a marked tendency as a polyisocyanate mixture enriched with 4,4'-diisocyanate diphenylmethane to form sediment containing uretdione groups at temperatures in a range from 40 to 150° C.

The diisocyanate mixture A obtained from the starting product is fractionated in a multiple stage column under a reflux of from 0.5:1 to 20:1, the 2,2'- and 2,4'-isomers preferentially distilling over with the fraction

C (first runnings), leaving behind a fraction D with the 4,4'-isomer. A vacuum at the head of the column of from 0.2 to 4 Torr is required for this distillation. Even when using columns which have limited pressure losses, for example columns with packings of profiled steel plate or helical springs or with wire-gauze packings, and evaporators with little or no pressure losses are used, a boiling point above 150° C (at which 4,4'-diisocyanato diphenylmethane decomposes to form carbodiimides) is adjusted at the sump of the column. After fractionation, the sump product E always contains polymer which is separated off from pure 4,4'-diisocyanato diphenylmethane by another distillation using a falling-film evaporator. The sump product E, usually amounting to less than 5% by weight of the diisocyanate used, remains liquid with a monomeric diisocyanate content of more than 50% by weight. It is suitable for the production of polyurethane plastics, if desired in admixture with first runnings C and concentrate B.

Fractionation of the diisocyanate mixture A can be combined with a treatment with iron chloride which is used to convert chlorine-containing impurities into a non-volatile form. The fractionation column may also be preceded by a distillation vessel operated in a vacuum of from 3 to 20 Torr. The object of the distillation is to remove traces of solvents which would interfere with the higher vacuum which is used in the fractionation column. The distillation vessel also acts as a container in which iron chloride is brought into contact with the chlorine-containing impurities at temperatures above 150° C.

Several fractionation columns can be arranged in series, in which case the following column is filled with head product from the preceding column, and the sump product mixed with the material running into the preceding column. This arrangement enables each column to be operated with a lower pressure loss, i.e. at a lower sump temperature, because the number of necessary separation units is distributed over several columns. It also enables polymer formation from the isocyanate to be reduced.

It is best to operate all this apparatus on a continuous cycle in order to keep the first runnings, the pure distillate and the polymer uniform in quality.

With fraction C, it is possible under favourable conditions to separate more than 90% by weight of the 2,2'- and 2,4'-isomers in a single distillation stage, depending upon how the columns are operated and arranged. However, if an increase in concentration which can be obtained in a column with more than 50 theoretical plates or a reflux ratio of greater than 10:1 is obtained, there is an increase in the residence time and in the sump temperature which is usually governed by the differen-

tial pressure in the column and hence in polymer formation and in the losses of 4,4'-diisocyanato diphenylmethane. Hence distillation in columns arranged one after the other is preferred. It is possible by repeated fractionation to obtain the 2,2'- and 2,4'-isomers having a purity of more than 95% by weight.

The fraction D has a 4,4'-diisocyanato diphenylmethane content of at least 98% by weight and can be processed so that it has a 4,4'-diisocyanato diphenyl methane content of more than 99% by weight, again depending upon the method of operation. A product as pure as this cannot be obtained directly by condensing aniline and formaldehyde, phosgenating the product of condensation, distilling off the product of condensation and distilling off the diisocyanate.

In order to mix concentrate B with the first runnings C, it is possible to collect the concentrate B immediately after it has been prepared in a vessel containing first runnings C from the separation of the isomers or continuously to mix it with the first runnings C accumulating from separation of the isomers and to obtain the required setting in this way. It is also possible in the process according to the invention to mix only part of the concentrate B with the first runnings C and to obtain a product which contains more diisocyanate and which is more free-flowing than the polyisocyanate mixture used for distillation.

The 2,2'- and 2,4'-diisocyanato diphenylmethane introduced in the first runnings C provides the mixture (III) with properties which are advantageous in many respects. Since 4,4'-diisocyanato diphenylmethane is usually the predominating constituent of the starting material, this compound initially crystallises on cooling. The exchange of 4,4'- for 2,2'- and 2,4'-isomers improves the resistance of the mixture to low temperatures.

Another advantage of the process according to the invention is that it enables the isomer content of the end products to be adjusted and kept very uniformly to the required level. For example, the amount of 2,4'- in 4,4'-diisocyanato diphenylmethane can be kept under $1\% \pm 0.2\%$.

In aromatic polyisocyanates, NCO groups in the ortho-position react more slowly with hydroxyl compounds than NCO groups in the para-position. Accordingly, the polyisocyanate mixtures (III) according to the invention enriched with 2,2'- and 2,4'-isomers are eminently suitable for the production of polyurethane lacquers whose pot-life is longer than that of lacquers which have a higher 4,4'-isomer content, for the above reason. Since the viscosity of the polyisocyanate mixtures (III) according to the invention can be adjusted by the quantity of 2,2'- and 4,4'-isomers added, the mixtures (III) according to the invention represent interesting starting materials for the production of foams. For example,

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they can be used to produce foams in moulds and by using the flow properties of the material these can readily be adapted to the moulds. The polyisocyanate mixtures (III) according to the invention are also suitable for the production of core sand binders, sealing compositions, coatings and other materials.

4,4'-Diisocyanato diphenylmethane of low isomer content (II) according to the invention is an excellent starting material for the production of elastic fibres, homogeneous and microporous coatings and elastomers and the invention extends to such materials.

Polyphenyl - polymethylene - polyisocyanato mixtures (III) are excellent starting materials for polyurethane (urea) lacquers, coatings, films, foams, foundry core binders and sealing compositions, and the invention extends to such materials.

The following Examples illustrate the invention (in these examples, percentage contents are by weight, unless otherwise specified):—

Example 1.

A polyisocyanate mixture (viscosity 100 cP/25° C) containing 3.5% of 2,4'-diisocyanato diphenylmethane,

59.4% of 4,4' - diisocyanato diphenylmethane,

1.2% of 1 - (4 - isocyanato phenylmethyl) - 3 - (2 - isocyanato phenylmethyl) - 4 - isocyanato benzene,

20.6% of 1,3 - di - (4 - isocyanato phenylmethyl) - 4 - isocyanato benzene, and

8.6% of tetranuclear isocyanates,

is separated in a falling-film evaporator into a fraction A containing 0.1% of 2,2' - diisocyanato diphenylmethane,

5.1% of 2,4' - diisocyanato diphenylmethane, and

94.7% of 4,4' - diisocyanato diphenylmethane,

and a polyisocyanate mixture (fraction B) with a viscosity of 800 cP/25° C. The diisocyanate mixture to which 200 ppm of ferric chloride are added passes continuously through a distillation column or gas-separation column, a fractionation column (Montz/Kloss system) with an exchange height of 17 metres and a falling-film evaporator of the Sambay type.

The object of gas separation carried out under a vacuum of 8 Torr and at a temperature of 200° C is to remove small quantities of chlorobenzene remaining from the phosgenation process. In the column, an isomer mixture containing 0.4% of 2,2'-, 22.0% of 2,4'- and 77.6% of 4,4'-diisocyanato di-

phenylmethane is run off under a vacuum of 3 Torr at the head of the column and at a sump temperature of 210° C (reflux ratio 4:1).

For evaporation, a stream of the sump product is pumped through a vertically arranged steam-heated tubular heat exchanger by means of a rotary pump arranged at the bottom of the column. A second stream from the same pump is delivered to a similarly steam-heated falling-film evaporator in which it is separated into 4,4' - diphenylmethane diisocyanate (fraction D) and a sump product (E). The distillate is converted into a flaky product by means of a cooling roller. Analysis by gas chromatography shows that this product (II) contains 0.6% of 2,4'-diisocyanato diphenylmethane, solidified at 39.1° C and has a residual chlorine content of less than 20 ppm.

The sump product E which is viscous at room temperature is collected in a container from which it is added to the polyisocyanate mixture B (viscosity 800 cP/25° C).

Addition of 27 parts of fraction C from the fractionation column to 73 parts of the aforementioned polyisocyanate mixture B combined with the sump product E forms the end product with the following analytical data:

Viscosity 205 cP/25° C,

30.6% of NCO

0.15% of hydrolysable chlorine,

0.39% of total chlorine,

74 ppm of iron,

7.4% of 2,4' - diisocyanato diphenylmethane,

53.2% of 4,4' - diisocyanato diphenylmethane,

1.1% of 1 - (4 - isocyanato phenylmethyl) - 3 - (2 - isocyanato phenylmethyl) - 4 - isocyanato benzene,

22.9% of 1,3 - di - (4 - isocyanato phenylmethyl) - 4 - (isocyanato benzene), and

6.5% of tetranuclear isocyanates.

This isocyanate is foamed with a polyol mixture consisting of 40% of a polyester with an OH number of 380, 30% of a polyether with an OH number of 380 and 30% of a polyether with an OH number of 550.

These polyethers were obtained by reacting a trifunctional alcohol with propylene oxide. The polyol mixture also contains 3% by weight of a 50% aqueous solution of the sodium salt of sulphonated ricinoleic acid, 1.2% by weight of a commercial polyether siloxane and 1% by weight of a tertiary amine. 100 Parts of the mixture are reacted with 130 parts by weight of the above isocyanate following the addition of 40 parts by weight of fluorotrichloromethane in an HK spraying machine, model 100 (System Bayer).

The following reaction times are observed:

Starting time	Setting time	Expanding time
8	70	120 seconds

- 5 A closed-cell hard foam with a unit weight of 23 kg/m³ is obtained. This foam remains dimensionally stable after storage for 1 hour at -10° C.

Example 2.

- 10 This example compares the results obtained using polyisocyanate mixtures which have been prepared from a uniform polyisocyanate mixture obtained by phosgenation of a polyamine mixture obtained by aniline/formaldehyde condensation. By distilling off
15 various quantities of diisocyanate, polyiso-

cyanate mixtures with reduced diisocyanate contents are obtained. Isocyanate mixtures of comparable viscosity are produced from these polyisocyanate mixtures of reduced diisocyanate content by mixing again with diisocyanate. The results are given in the table, in which:

X refers to diisocyanate as obtained from the distillation without accumulation of the 2,4'-isomer, and

Y refers to diisocyanate as obtained by fractional distillation of X as the head product with enriched 2,4'-isomers.

Z refers to an isocyanate mixture which was adjusted to the desired viscosity simply by distilling off diisocyanate and to which no diisocyanate has been added.

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Isocyanate Mixture No.:	1	2	3	4	5	6	7	8
Viscosity cps/250 after distilling off diisocyanate (= stock)	435	1250	1250	200	435	435	1250	1250
Mixed with diisocyanate	Y*	Y*	X	Z	X	Y*	X	Y**
Ratio, Stock : diisocyanate	74:26	63:37	63:37	100:0	85:15	85:15	73:27	73:27
Viscosity of the mixture cps: 25°C	124	118	115	200	180	185	210	188
2,4'-diisocyanate % by weight	11.7	15.2	2.2	1.4	1.3	6.7	2.3	12.4
4,4'-diisocyanate % by weight	44.4	38.9	50.3	45.2	50.2	42.3	46.2	35.8
3-Nuclear isocyanate I % by weight (3 K I)	1.0	0.9	0.9	1.4	1.2	1.2	1.1	1.2
3-Nuclear isocyanate II % by weight (3 K II)	18.2	19.2	19.3	25.7	22.8	22.8	21.8	22.1

* Content 40% 2,4'-isomers by weight

** Content 50% 2,4'-isomers by weight

Ratio:

2,4' : 4,4' (- a)	0.263	0.391	0.044	0.031	0.026	0.158	0.050	0.347
3 n I : 3 n II (- b)	0.055	0.047	0.047	0.055	0.053	0.053	0.050	0.054
a : b	4.8	8.3	0.9	0.6	0.5	3.0	1.0	6.4

Example 3.

This comparison example refers to isocyanate mixtures Nos. 2 and 3 of the preceding example, which are processed after addition of 0.2% by weight each of isophthalyl chloride with a polyol component to give a coating composition.

Polyol component

1200 Parts by weight of a polyether com-

Titanium dioxide (rutile type)	800 parts by weight
Quartz powder (0.03 to 0.2 mm)	5300 parts by weight

pound which has an OH content of 11.5% and a viscosity of 700 cps (25° C) produced by reacting propylene oxide with trimethylol propane are mixed with 2200 parts by weight of castor oil first pressing (OH content 4.8%), 500 parts by weight of sodium aluminium silicate of the zeolite type are dispersed in this mixture. The sodium aluminium silicate used has a water content of <2.5%. The following are used as further components of the mixture:

This batch is homogenised with a mechanical agitator for twenty minutes and degasified in a vacuum unit at a pressure of 30 Torr for ten minutes. The product thus produced is the component I of a solvent-free coating composition.

For testing the pot-life, 100 parts by weight of the batch are removed and mixed with 23 g of polyisocyanate. A free-flowing mass is obtained which can be processed by casting and solidifies within 24 hours to a hard plastic. A comparison test shows that the pot-life with the isocyanate mixture No. 2 is seventy minutes. With the isocyanate mixture No. 3, however, the pot-life is only forty minutes.

WHAT WE CLAIM IS:—

1. A process for the production both of (II) at least 98% by weight pure 4,4'-diphenylmethane diisocyanate and (III) a polyphenyl-polymethylene-polyisocyanate mixture from a polyisocyanate mixture (I) which has been obtained by condensation of aniline and formaldehyde, followed by phosgenation of the condensation product, wherein the polyisocyanate mixture (I) is separated by fractional distillation into a fraction A which consists mainly of isomeric diphenylmethane diisocyanates, and a fraction B which, in addition to isomeric diphenylmethane, diisocyanates, consists of polyisocyanates containing more than two aromatic nuclei, and in which fraction A is then separated by fractional distillation into a fraction C consisting of 2,2', 2,4'- and 4,4'-diphenylmethane diisocyanates, and a fraction D at least 98% by weight of which consists of 4,4'-diphenylmethane diisocyanate and into a residue E comprising material formed as a result of high temperature polymerisation and in which fraction C is mixed with at least part of fraction B to produce a mixture having a K-value (as herein

defined) of greater than 1.3 which mixture is product (III); the product (II) being fraction D.

2. A process as claimed in claim 1 in which the polyisocyanate mixture (I) used contains 40 to 80% by weight of diisocyanate which has a 2,4'-isomer content of 1 to 40% by weight.

3. A process as claimed in claim 2 in which the mixture (I) contains 50 to 70% diisocyanate by weight and 4 to 8% by weight of 2,4'-isomers.

4. A process as claimed in any of claims 1 to 3 in which up to 70% by weight of the diisocyanate is distilled off in fraction A.

5. A process as claimed in any of claims 1 to 4 in which fractionation of the diisocyanate mixture A is combined with a treatment with an iron salt to remove chlorine-containing impurities.

6. A process as claimed in any of claims 1 to 5 in which fraction C is mixed not only with at least part of fraction B but also with residue E to give product (III).

7. A process as claimed in claim 1 substantially as herein described with reference to any one of the Examples.

8. Product II which contains at least 98% by weight of 4,4'-diphenylmethane diisocyanate when produced by a process as claimed in any of claims 1 to 7.

9. A polyphenyl-polymethylene-polyisocyanate mixture (III) when prepared by a process as claimed in any of claims 1 to 7.

10. Polyurethane (urea) elastomers, fibres, films, foams and microporous sheets when produced using 4,4'-diisocyanato diphenylmethane as claimed in claim 8.

11. Polyurethane (urea) lacquers, coatings, films, foams, foundry core binders and sealing compositions when produced using a polyphenyl-polymethylene-polyisocyanate mixture (III) as claimed in claim 9.

ELKINGTON AND FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London W.C.1,
Agents for the Applicants.

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